and decomposes only a little more slowly than it is formed. The resultant material was a mixture of the oxide and hyponitrite from which the hyponitrite could not be separated. The hyponitrite was identified by its nitrosyl band at 1690 cm.$^{-1}$ and an absorption band at 1080 cm.$^{-1}$ due to the hyponitrite group.[12]

The important infrared frequencies are listed in Table II along with those of other nitrosyl nickel compounds. The nitrosyl frequency is strongly dependent upon the coordinated ligands. A similar effect has been studied with metal carbonyls.[13] However, since the nitrosyl frequency is quite as dependent upon the anion (1735–1680 cm.$^{-1}$) as it is upon the phosphine (1855–1735 cm.$^{-1}$) (see also ref. 9), it is difficult to invoke the usual explanation of the back donation (π-bonding) by the metal to account for these frequency shifts. An alternative explanation is that the bonding between the nitrosyl group and the nickel atom is strongly dependent upon the relative energies of the d-orbitals of the nickel, which in turn are strongly affected by the surrounding ligand field. This is a subject which requires extensive investigation of a much wider range of metal nitrosyl complexes.

Acknowledgment.—The author wishes to thank Dr. L. Vaska for the magnetic measurements.

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[12] L. Kuhn and E. R. Lippincott, *J. Am. Chem. Soc.*, **78**, 1820 (1956).

[13] M. Bigorgne, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 199.

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Metal Nitrosyls. II. The Reaction of Nitric Oxide with Dicarbonylbis(triphenylphosphine)nickel[1]

BY ROBERT D. FELTHAM

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The reactions of nitric oxide with $Ni[CO]_2[(C_6H_5)_3P]_2$ and $Ni(CO)_3(C_6H_5)_3P$ are shown to lead to a variety of nitrosyl nickel compounds of the type $NiX(NO)L_2$. L is triphenylphosphine or solvent ligand and X^- includes $^1/_2O^{2-}$, OH^-, $^1/_2N_2O_2^{2-}$ NO_2^-, and CH_3O^-. Molecular weights show them to be four-coordinate.

The reaction between nickel carbonyl and nitric oxide has been investigated by several authors.[2–4] From some of our own preliminary experiments, it was clear that this reaction leads to a mixture of unstable products. In order to stabilize these complexes, the reaction was carried out between nitric oxide and triphenylphosphine carbonyl nickel complexes.

Experimental

The infrared spectra were run as Nujol and halocarbon mulls on a Beckman IR-4 spectrophotometer. Molecular weights were determined under nitrogen using a Mechrolab Model 301A vapor pressure osmometer or ebullioscopically in benzene. Elemental analyses were performed by the Huffman Microanalytical Laboratories, Wheatridge, Colorado. All oxygen analyses reported here were determined directly using the Untersaucher method. Analyses for N_2, NO, CO, N_2O, and CO_2 using gas–solid chromatography[5] were carried out by the Physical Measurements Laboratory of this Institute.

Materials.—Triphenylphosphine was obtained from the M and T Corp. and recrystallized from ethyl acetate. Nickel carbonyl, as obtained from the International Nickel Company, was used without further purification.

The nitric oxide as obtained from Matheson contained 1.5% N_2O, 0.2% CO_2, 1% N_2, and traces of NO_2. In order to remove all of the NO_2 as well as some of the other impurities, the nitric oxide was passed slowly over $^1/_{16}$-in. pellets of Molecular Sieve No. 5A (Linde Company) at $-78°$. It was found that this treatment removed all impurities except N_2 and traces of N_2O. Simply passing NO over NaOH does not adequately remove NO_2. The nitrogen used as inert atmosphere was the "H.P. Dry" grade as obtained from the Linde Company.

Dicarbonylbis(triphenylphosphine)nickel, $Ni[CO]_2[(C_6H_5)_3P]_2$, was prepared as described by Rose.[6] The compound was recrystallized from ethyl acetate and dried under vacuum. The complex was a white crystalline solid, m.p. 210° dec. (reported[6] m.p. 210–215° dec.). The infrared spectrum consisted of two bands at 2000 and 1935 cm.$^{-1}$ in the carbonyl region.

Tricarbonyltriphenylphosphinenickel, $Ni(CO)_3(C_6H_5)_3P$, was prepared using the method described by Meriwether[7] and was found to have bands at 2080 and 1920 cm.$^{-1}$ in the infrared region. $Ni(CO)_3(C_6H_5)_3P$: color, white. *Anal.* Calcd.: Ni, 14.45. Found: Ni, 14.46.

Reactions with NO.—All operations were carried out under nitrogen and all reagents were carefully dried. The nickel complex to be used was placed in a round bottom flask of appropriate size and the solvent was added. The flask was evacuated to the vapor pressure of the solvent at room temperature (25°), and nitric oxide was added without stirring the solution until the pressure in the flask was equal to atmospheric pressure. The supply of NO was then shut off and the solution was magnetically stirred. Using this technique, the mole ratio of NO to Ni could be carefully controlled.

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[1] Presented in part at the 7th International Conference on Coordination Chemistry, Stockholm, Sweden, June, 1962. This work was sponsored by The International Nickel Company, Inc.

[2] H. Reihlen, A. Gruhl, G. v. Hessling, and O. Pfrengle, *Ann.*, **482**, 161 (1930).

[3] J. C. W. Frazer and W. E. Trout, *J. Am. Chem. Soc.*, **58**, 2201 (1936).

[4] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

[5] M. Lefort and X. Tarrago, *J. Chromatog.*, **2**, 218 (1959).

[6] J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

[7] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

In a few cases, leaks developed in the system as evidenced by the slight yellow coloration of the gas due to the presence of NO_2. The concentration of NO_2 was estimated from the color of the gas. As a reactant, it was present in minor quantities (about 0.01% of the nickel added). However, the presence of NO_2 determined the composition of the nitrosyl nickel compounds formed from these reactions.

(1) Dicarbonylbis(triphenylphosphine)nickel (1.00 mmole) was treated with 1.86 mmoles of NO in 100 ml. of CCl_4 for 24 hr. At the end of this time, a white, insoluble solid and a dark blue solution were obtained. The white solid was separated from the solution by filtration, and the filtrate was evaporated at room temperature under vacuum to a volume of 20 ml. After standing for several days, 0.284 g. of a blue crystalline solid was filtered off. This compound had an NO band at 1710 cm.$^{-1}$. Another small amount (0.061 g.) of this product was obtained by adding 20 ml. of *n*-hexane to the filtrate, giving a total yield of 0.345 g., or 55% based on the nickel added. During recrystallization from benzene–*n*-hexane, this compound reacted with water and was converted to $Ni(OH)(NO)[(C_6H_5)_3P]_2$.

$Ni(OH)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 68.60; H, 4.96; N, 2.22; Ni, 9.31; O, 5.08; P, 9.83; mol. wt., 630. Found: C, 68.73; H, 4.62; N, 1.96; Ni, 9.44; O, 6.35; P, 9.0; mol. wt., 500 (in benzene).

(2) Dicarbonylbis(triphenylphosphine)nickel (3.00 mmoles) in 250 ml. of dry oxygen-free ethyl acetate was magnetically stirred together with 5.7 mmoles of nitric oxide for about 4 hr. Analysis of the gases showed that about 1.6 mmoles of nitric oxide had reacted, while 1.7 mmoles of carbon monoxide and 0.5 mmole of nitrous oxide were evolved. After filtering, the solution was evaporated to 125 ml. and 0.3 g. (33% based on the amount of Ni reacted) of a dark blue solid crystallized out. This product was identical in all respects with that obtained from the reaction in CCl_4 (see above). The compound as first obtained had an NO band at 1710 cm.$^{-1}$, but hydrated rapidly in the air to give another compound with a slightly different NO band at 1720 cm.$^{-1}$ and a new band due to water at 3400 cm.$^{-1}$.

$Ni(OH)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: N, 2.22. Found: N, 2.44.

(3) Dicarbonylbis(triphenylphosphine)nickel (1 mmole) was slurried in 100 ml. of *n*-hexane together with 1.96 mmoles of NO for 2 days. At the end of this time, a dark blue solid had formed and was filtered off. An infrared spectrum showed this to be a mixture of unreacted starting material and nitrosyl complexes with NO bands at 1710 and 1680 cm.$^{-1}$. The nitrosyls could not be separated from the starting material by recrystallization; therefore no analyses were obtained.

(4) In the presence of NO_2 dicarbonylbis(triphenylphosphine)nickel reacted with NO under conditions otherwise identical with those described (see 1 above) to give a different compound. In the presence of NO_2 almost all of the nitric oxide had reacted with the nickel complex. After recrystallization from benzene–*n*-hexane, a compound was obtained containing one mole of benzene per mole of complex and having a nitrosyl band at 1745 cm.$^{-1}$.

$Ni(NO_2)(NO)[(C_6H_5)_3P]_2 \cdot C_6H_6$: color, blue. *Anal.* Calcd.: C, 68.41; H, 4.90; N, 3.80; Ni, 7.96; O, 6.51; P, 8.41; mol. wt., 737. Found: C, 67.95; H, 4.96; N, 3.86; Ni, 8.20; O, 6.65; P, 8.2; mol. wt., 700 (in benzene).

If, instead, the complex was recrystallized from ethyl acetate, no solvent was present in the crystals and the nitrosyl frequency was 1730 cm.$^{-1}$.

$Ni(NO_2)(NO)[(C_6H_5)_3P]_2$: color, blue. *Anal.* Calcd.: C, 65.58; H, 4.59; N, 4.25; Ni, 8.90; O, 7.28; P, 9.4; mol. wt., 659. Found: C, 65.25; H, 4.68; N, 4.13; Ni, 8.74; O, 7.53; P, 9.3; mol. wt., 673 (in benzene).

(5) Tricarbonyltriphenylphosphinenickel was slurried in 50 ml. of *n*-hexane and NO was bubbled through the mixture for 1 hr. The blue solid which had formed was filtered off and washed with 200 ml. of *n*-hexane. This material was then extracted with methanol using a Soxhlet extractor. A dark purple solid crystallized from the hot methanol, giving 2.5 g. of a compound with the approximate composition $Ni(OCH_3)(NO)(C_6H_5)_3P \cdot 2CH_3OH$. This compound was dried at 100° under vacuum (0.01 mm). The equivalent weight was determined by treating the product with excess 1 *N* HCl in 95% ethanol and titrating the residual hydrochloric acid with lithium hydroxide.

$Ni(OCH_3)(NO)(C_6H_5)_3P \cdot 2CH_3OH$: color, dark purple. *Anal.* Calcd.: C, 57.90; H, 5.68; N, 3.38; Ni, 14.14; O, 11.54; P, 7.47; equiv. wt., 447. Found: C, 56.18; H, 4.59; N, 3.14; Ni, 13.32; O, 14.32; P, 7.15; equiv. wt., 453.

Results and Discussion

There were several difficulties encountered with these reactions. First, it was found that even traces of nitrogen dioxide drastically altered the course of the reaction of dicarbonylbis(triphenylphosphine)nickel with nitric oxide. Consequently, the nitric oxide was carefully purified as described above. Second, accurate oxygen analyses were needed to distinguish among the many possible products from this reaction. Fortunately, it was found that in these compounds, the presence of nickel and phosphorus does not interfere with oxygen analyses. Third, several unstable or reactive compounds result from this reaction.

In the experiment described above with *n*-hexane as the reaction medium, a mixture of two nitrosyls was obtained with NO absorptions at 1710 and 1680 cm.$^{-1}$. The nitrosyl complex with a frequency of 1680 cm.$^{-1}$ was observed in every other solvent used including benzene, ethyl acetate, and carbon tetrachloride, if the reaction mixture was not allowed to stand for more than 1 or 2 hr. After standing for longer periods of time in these solvents, this mixture of nitrosyl complexes slowly loses nitrous oxide and only the single nitrosyl compound with its NO band at 1710 cm.$^{-1}$ could be isolated. This compound was very hygroscopic, being rapidly converted to $Ni(OH)(NO)[(C_6H_5)_3P]_2$ with an NO band at 1720 cm.$^{-1}$. This mixture of compounds was similar to that obtained from the reaction of $Ag_2N_2O_2$ with $NiBr(NO)[(C_6H_5)_3P]_2$.[8] Thus, the two nitrosyls formed were the hyponitrite (1680 cm.$^{-1}$) and the oxide (1710 cm.$^{-1}$), with the oxide resulting from the loss of N_2O by the hyponitrite.

In the experiments where the nitric oxide was contaminated with NO_2, a single stable nitrosyl compound resulted. This compound appears to be identical with the compound described by Griffith, Lewis, and Wilkinson[9] as a dinitrosyl which was characterized by a single NO absorption at 1745 cm.$^{-1}$. Our elemental analysis showed there to be three oxygens per nickel. This agrees well with the oxygen as determined by difference from the data of the other authors.[9] Therefore the compound must be $Ni(NO_2)(NO)[(C_6H_5)_3P]_2$. The conclusion based on elemental analysis that this compound is a nitrosyl nitrite is clearly confirmed by its infrared spectrum. The presence of a single NO band (1745 cm.$^{-1}$) along with strong absorptions at

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(8) R. D. Feltham, *Inorg. Chem.*, **3**, 116 (1964).

(9) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 2259 (1961).

1380 and 1105 cm.$^{-1}$ is consistent for a compound with one NO group and a coordinated nitrito group.[10] It is also identical with the compound obtained from the reaction of $AgNO_2$ with $NiBrNO[(C_6H_5)_3P]_2$.[8]

When nitric oxide at atmospheric pressure was treated with $Ni(CO)_3(C_6H_5)_3P$ in hexane and then extracted with methanol, the compound $Ni(OCH_3)(NO)(C_6H_5)_3P \cdot 2CH_3OH$ resulted. The compound was found to consume one equivalent of H^+ per mole of nickel, thus leading to its formulation as the monomethoxide. The air-sensitive dark purple compound is very similar to the bis(triphenylphosphine)nitrosylnickel compounds described above. Its NO absorption (1715 cm.$^{-1}$) is almost identical with that of $Ni(OH)(NO)[(C_6H_5)_3P]_2$, while all other features of the infrared spectra are due to triphenylphosphine or methanol.

Conclusions

The reaction of nitric oxide with all of the nickel(0) compounds used in these experiments leads to complexes of $(NiNO)^+$. The complexity of the system is thus due to the presence of a variety of more or less stable anions. The anions which have been identified as resulting from this reaction are $N_2O_2^{2-}$, O^{2-} (or OH^-), OCH_3^-, and NO_2^-. No evidence could be found for the presence of NO_3^-, $N_2O_3^{2-}$, CO_3^{2-}, or HCO_3^-.

The primary reaction in the absence of NO_2 is

$$4NO + 2Ni(CO)_2[(C_6H_5)_3P]_2 \longrightarrow (NiNO[(C_6H_5)_3P]_2)_2N_2O_2 + 4CO \quad (1)$$

followed by

$$(NiNO[(C_6H_5)_3P]_2)_2N_2O_2 \longrightarrow N_2O + (NiNO[(C_6H_5)_3P]_2)_2O \quad (2)$$

The oxide reacts with water (or alcohol)

$$(NiNO[(C_6H_5)_3P]_2)_2O + H_2O \longrightarrow 2Ni(OH)(NO)[(C_6H_5)_3P]_2 \quad (3)$$

In the presence of NO_2, one gets only the nitrite

$$Ni(CO)_2[(C_6H_5)_3P]_2 + 4NO \xrightarrow{NO_2} NiNO_2(NO)[(C_6H_5)_3P]_2 + N_2O \quad (4)$$

The stoichiometry of reactions 1 and 2 has been quantitatively confirmed by gas–solid chromatography of the residual gases from these reactions. Reaction 4 has been established by the isolation and analysis of nitrito bis(triphenylphosphine)nitrosylnickel.

No stable dinitrosyls were formed during these reactions as had been reported earlier,[9] although their existence as unstable intermediates is suggested both by the stoichiometry and by the isolation of an unstable nitrosyl hyponitrite from the reaction.

Acknowledgments.—The author wishes to thank Frank Kabot and Robert Reitz of the Physical Measurements group of this Institute for the chromatographic analysis of these gases, and especially Earle Hewitt for his experimental assistance.

[10] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Metal Nitrosyls. III. The Reaction of Nitric Oxide with Nickel Carbonyl[1]

BY ROBERT D. FELTHAM AND JONATHAN T. CARRIEL

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The reaction of nitric oxide with nickel carbonyl in polar and nonpolar solvents leads to a variety of compounds derived from the species $[NiNO]^+$. When this reaction is carried out in the presence of cyclopentadiene there is almost complete conversion to nitrosylcyclopentadienylnickel.

Other workers in this field have variously described the complexes obtained from the reaction of nitric oxide with nickel carbonyl in polar solvents (particularly methanol and ethanol) as being $[NiNO]^+$ (ref. 2), $[NiNO]^{2+}$ (ref. 3), or $[NiNO]^{3+}$ (ref. 4). The two main difficulties encountered by earlier workers were (1) under their conditions a mixture of salts of $[NiNO]^+$ was obtained and (2) in the absence of stabilizing ligands these compounds slowly decompose.

The results from the reaction between nitric oxide and phosphine-substituted nickel carbonyls[5] suggest that these difficulties might be overcome by rapid reaction at superatmospheric pressure.

Experimental

Apparatus and Materials.—For the high pressure reactions a 1-l. "Magnedash" autoclave with a glass liner was used. The nickel carbonyl was used as supplied by The International Nickel Company, Inc. The nitric oxide supplied by Matheson was cooled to −78° in a Dry Ice trap to remove the traces of NO_2 which are present in the nitric oxide. All the solvents and amines used were dried over $^1/_{16}$-in. pellets of Linde Molecular Sieve No. 4A. Enjay dicyclopentadiene was cracked to the monomer at 260° and stored at −78°. The gases were analyzed by gas–solid chromatography,[6] while $Ni(CO)_4$ was analyzed by gas–liquid chromatography using a 3-m. column containing 15% P.E.G. 1500 supported on 30–60 mesh firebrick at 78° with a helium flow of 48 ml./min. All elemental analyses were done by

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[1] This research was sponsored by The International Nickel Company, Inc.

[2] J. S. Anderson, *Z. anorg. allgem. Chem.*, **229**, 357 (1936).

[3] H. Reihlen, *ibid.*, **230**, 223 (1937).

[4] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1775 (1959).

[5] R. D. Feltham, *Inorg. Chem.*, **3**, 119 (1964).

[6] M. Lefort and X. Tarrago, *J. Chromatog.*, **2**, 218 (1959).